

CHEMISTRY

Vibration Frequency and Ionization Potential: Halide Molecules

It has been observed that a systematic correlation is possible between the sum of normal vibration frequencies of a molecule and the first ionization potentials of its constituent atoms.

The sum, $\Sigma\nu$, of all the normal frequencies (degeneracies, if any, included) of a molecule RX_n , where X is a halogen and R a molecular group, has been found to be a linear function of the sum of the first ionization potentials, ΣI_x , of the halogen atoms occurring in the molecule. A plot of $\Sigma\nu$ for a group of molecules with the same R , but with all possible halogen substitutions against ΣI_x , is thus a straight line. Preliminary tests, indicating the validity of the relation, have been made on fifteen CX_4 , nine CHX_3 , six CH_2X_2 , four CH_3X , nine C_2X_4 , seven C_2HX_3 , five $C_2H_2X_2$, three C_2H_3X , ten $^{11}BX_3$, ten $^{10}BX_3$ and three XCN type molecules.

It is also observed that the $\Sigma\nu$ values of two similar sequences of halides are linearly related:

$$\Sigma\nu(R'X_n) = \alpha\Sigma\nu(RX_n) + \beta$$

provided both the series contain the same number of halogens and the corresponding members are compared.

Details of the work and results of allied investigations will be reported elsewhere.

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Delayed Gas Evolution from Passive Films formed in the Kolbe Reaction

DURING the course of electrochemical kinetic studies on the Kolbe reaction, we have observed a remarkable phenomenon, the details of which are recorded here. The classical Kolbe reaction involves the anodic electrolytic synthesis of hydrocarbons from solutions of salts of appropriate aliphatic carboxylic acids. As a model system for preliminary investigations of the electrochemical kinetics of this reaction, we have examined the anodic reaction which occurs in the electrolysis of a solution of potassium formate in pure anhydrous formic acid; in this case 1 mole of carbon dioxide is evolved in the passage of two Faradays.

During steady-state electrolysis of the above solution at platinum, gold and palladium electrodes, the only gas evolved is carbon dioxide. The overall reaction is hence formally¹:



On interrupting the current at platinum and gold electrodes, the gas evolution ceases immediately in the normal way. However, on interrupting the current at a palladium electrode, the gas evolution initially ceases, but is then followed by a further burst of gas from the surface after a delay period of up to 5 sec., this gas evolution occurring in the complete absence of current-flow. The effect at palladium is quite reproducible and is best observed at a current density greater than 10^{-1} amp./cm.² in 5-M solutions of potassium formate in formic acid (pre-saturated

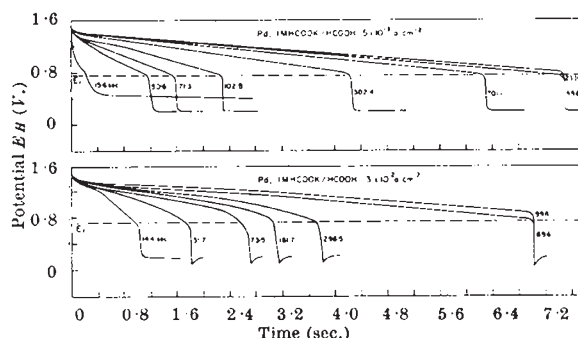


Fig. 1. Open-circuit e.m.f. decay curves taken on an oscilloscope at two current densities of prior polarization for the indicated times (sec.).

with carbon dioxide) at 5° C. Although carbon dioxide is evolved at platinum and gold with the same current efficiency (about 90 per cent) as at palladium, the delayed gas evolution is not observed, and the effect hence arises from some property of the palladium anode. No hydrogen is evolved as might be expected by analogy with the coupling reaction occurring with acetic and other aliphatic acids, but this is understandable since any H radicals generated by the anodic decarboxylation will ionize rapidly at a rate of at least 10^{10} amp./cm.² at the high anodic potentials (about 1.2 V. with respect to the hydrogen electrode in the same acid solution) required for significant rates of electrolysis of the formic acid. Hence it is improbable that hydrogen produced in the decarboxylation step and taken up into the surface regions of the palladium is responsible for the effect, and in fact the coulombic yields of carbon dioxide gas by continuous and repeatedly interrupted polarization are identical within experimental error and no hydrogen is detectable by chemical or gas chromatographic means under either set of conditions of polarization.

Rapid ciné-photography of the palladium surface with a simultaneous recording of the moment when current stops flowing has enabled the delay-times in gas evolution in interrupted polarization experiments to be measured with some precision to about 0.1 sec. The delay-time in the gas evolution after the current stops is found to be a function of the time of previous anodic electrolysis up to periods of about 5 min. This suggests that the anodic electrolysis

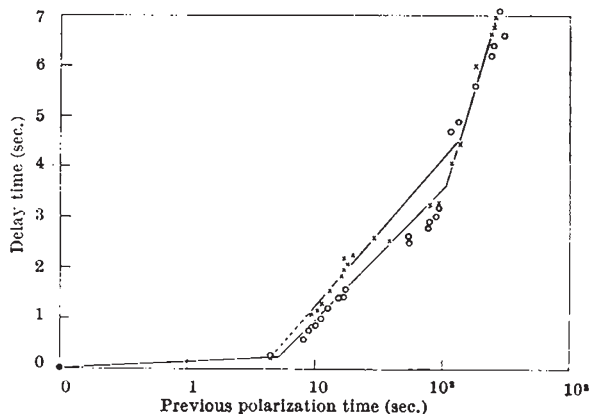


Fig. 2. Relationship of both the delay in open-circuit gas evolution (from ciné photography) and the potential delay to the period of prior anodic polarization at 10^{-2} amp./cm.². O, delayed gas evolution; x, potential delay; 5 M HCOOK/HCOOH